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Project Summary

Retention of Zinc, Cadmium, Copper, and Lead by Geologic Materials

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The vertical and horizontal migration patterns of zinc, cadmium, copper, and lead through the soil and shallow aquifer systems at a secondary zinc smelter were studied by the use of soil coring and monitoring-well techniques. The migration of metals that occurred was limited to relatively shallow depths into the soil profile by attenuation processes. Cation exchange and precipitation of insoluble metal compounds, as a result of pH changes in the infiltrating solution, were determined to be the principal mechanisms controlling the movement of the metals through the soil. Increased metals content in the shallow groundwater systems was confined to the immediate plant site.

Soil coring was an effective investigation tool, but not suitable by itself for routine monitoring of waste disposal activities. However, it should be used to gather preliminary information to aid in determining the proper horizontal and vertical locations for monitoring-well design. The analysis of water samples collected in this project generally did not provide an understandable pattern of results. A brief experiment on monitoring-well sampling indicated the need to develop reproducible sampling techniques to obtain representative water samples. The failure of some well seals in a highly polluted environment also indicates the need for additional research in monitoring well construction.

This Project Summary was developed by EPA's Hazardous Waste Engineering Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The primary purpose of this study was to verify in the field the effectiveness of glaciated region soils and associated surface deposits in retaining specific hazardous chemicals. The study also was designed to develop effective investigative and monitoring techniques for detecting and quantitatively evaluating the extent of groundwater pollution from surface waste disposal activities.

Special emphasis was placed on defining: 1) the vertical and horizontal migration patterns of chemical pollutants through the soil and shallow aquifer systems; and 2) the residual chemical buildup in soils in the vicinity of pollution sources.

Four industrial complexes were selected for study of the effects of their waste disposal practices on the soils and shallow groundwater systems. Site A, where most of the time, money, and effort was spent will be discussed.

Site A is a secondary zinc smelter located in south-central Illinois. The plant started operations between 1885 and 1890, initially processed zinc ore, and was converted to a secondary zinc smelting facility about 1915. Waste from the smelting operations during the first 85 years principally were heavy metals-rich cinders and ashes. During the early years large quantities of cinders were used as road fill or surfacing in the plant area. As a result of these disposal practices, there now is a 1- to 10-foot thick layer of metals-rich cinders covering about 12 acres of the plant property.

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In compliance with air pollution control regulations, a scrubber was installed on the plant stack in 1970. Prior to that time, wind-blown ash, rich in zinc and other heavy metals, was deposited on the plant site and on the surrounding farmland. This source of pollution has now been minimized, but wastewater from the scrubber is disposed of in a seepage pit constructed on the cinder materials that form the present-day land surfaces. Several hundred tons of high zinc content sludge have accumulated from the frequent cleaning of this pit and are being reprocessed for zinc recovery. Most of the water from the pit infiltrates into the ground underlying the plant property.

The collection of continuous vertical core samples for geologic study and chemical analyses, and the construction of piezometers or monitoring wells for water level measurements and water sampling were the principal field techniques used in this study.

Water level measurements were made and water samples were collected from each well once a month. Water samples were analysed for heavy metals at the Environmental Research Analytical Laboratory with zinc as the target element. Two electrochemical methods, anodic stripping voltammetry and pulse polarography, proved to be most effective for making zinc determinations and screening for the presence of other metals of interest. Total mineral analyses were also conducted.

Results

Altogether, 49 wells at 36 locations were completed at Site A. Core samples were taken at each of these locations and at an additional 23 sites. Total well and core sampling footages are about 1309 and 1454 feet respectively.

The glacial materials at the site range in thickness from about 55 feet on the east to about 75 feet on the west. The stratigraphic units recognized are essentially uniform in character and thickness and generally flat lying across the site. The elevation of the bedrock surface dips from 449 feet above sea level on the east to 432 feet on the west.

The expandable clay minerals, generally referred to as montmorillonite, make up more than 80 percent of the clay minerals within the Peoria Loess, Roxana Silt, and Berry Clay Member, thereby suggesting a high base exchange potential in the upper 13 feet of the materials encountered. The thin, continuous silty sand zone at the top of the Vandalia Till would appear to be the only permeable unit to allow groundwater to travel laterally at any moderate rate away from the site. Although there is probably some downward movement of groundwater through the remainder of the Glasford Formation, it would be expected to be extremely low.

On the basis of the geologic description of this site, it is quite obvious that no significant aquifer exists in the immediate vicinity of the plant site. The Hagarstown Member, a thin (1 to 2 feet thick) continuous silty sandy zone, appears to be the only permeable zone that could allow for significant lateral groundwater movement away from the site. To develop even a domestic water supply from this sand unit probably would require the construction of two or more large-diameter bored wells.

Water table contour maps show a water table mound beneath the plant complex. The relatively high permeability of the fill materials at the plant site, its topographic setting, and the liquid disposal activity at the plant all contribute to the development of this recharge mound.

No stabilized water levels were observed in some of the deep wells for the period of record. In general, water levels in the deep wells are higher than those in the shallow wells, indicating a probable upward movement of water within the glacial drift sequence. In the immediate plant area, where the shallow water levels are mounded, the movement of water in the shallow deposits probably is downward and horizontal. The average rates of groundwater movement from the mounded area were, for example, 0.17 ft/day in March 1976 and 0.19 ft/day in November 1975.

Chemical analysis of the core samples were conducted to define: 1) the vertical and horizontal migration patterns of chemical pollutants through the soil, and 2) the residual chemical buildup in soils in the vicinity of the pollution source. Preliminary analysis of core samples during the early stages of the study indicated that four elements (zinc, cadmium, copper, and lead) were most likely to be carried into the soils and groundwater system beneath the plant property. As a result these elements were selected for routine analyses.

Results of chemical analysis of core samples from the Site A control hole located approximately 3 miles south-southwest of the plant, and samples from unaffected soil horizons beneath the plant property suggest that background concentrations for the four elements tested should be about 20 to 50 ppm for zinc, 0.04 to 1.5 ppm for cadmium, 10 to 30 ppm for copper, and 10 to 40 ppm for lead. There appears to be no significant chemical variation with depth or between geologic unit boundaries. Some zinc levels in isolated Pleistocene soils were higher.

A series of cross sections for zinc, cadmium, copper, and lead concentrations of the soil were prepared to outline the limits of migration of these metals beneath the plant and give an indication of the effectiveness of the soils in retaining these metals. Small quantities of zinc were found in the upper 3 to 5 feet of the soil profile outside of the plant property. Most of the zinc introduced into this area probably was wind blown dust and ashes from the plant stack. The area of greatest accumulation and deepest concentration of zinc in the soil occurred immediately beneath the plant property.

The general shapes of the cross sections for cadmium, copper, and lead were similar to those for zinc. The depth of penetration of cadmium is slightly less than that of zinc but considerably greater than that of copper and lead.

The very shallow depths of penetration of these elements indicate the relative immobility of these metals. In general, the areas of greatest penetration of the four elements occurred beneath the scrubber wastewater pit. Here wastewater is a significant source of the metals and the recharge into the soil system is greatest. In other areas removed from the pit, the presence of the cinders became the dominant source of metals, and lowland areas where ponded water accumulates was the secondary source.

In addition to the direct percolation of metals-rich waste at the plant site, a significant amount of metals-rich surface water runs off the plant property and percolates into the stream beds draining the plant to the southwest and southeast. An accumulation of metals-rich cinder-type sediments in the stream bed was noted. The concentration of metal retained and depth of penetration decreases as the distance away from the plant site increases.

The mechanisms retaining the metals in the soil profile at Site A are predominantly cation exchange and precipitation of insoluble metal compounds as a result of pH change. Cation Exchange Capacity data generated indicate little variation in the retention capabilities of the upper geologic units, the silts, clays, and tills. Therefore, as metals-rich water percolates downward through the soil

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profile, the metals are exchanged preferentially in reverse order of their mobility.

Cation Exchange Capacities (CEC) of soils measured at Site A range from about 4 to 10 me/100 grams with the larger values occurring in the shallower soils. If zinc were transferred onto the available exchange sites of the soil, cation exchange could account for soil zinc concentrations up to about 3500 ppm. This value could be higher, according to some soil specialists, because the measured CEC may be lower than the original capacity of the soil. Some researchers maintain that the soil becomes "poisoned" in the presence of pollutants and true CEC values cannot be measured.

Aside from that possibility, three other factors may explain the difference between the very high soil zinc concentrations shown in the upper part of the soil profiles and the values attributable to cation exchange:

1) Some of the very high values obtained for the surface and near surface samples actually are chemical analyses of cinder fill samples.
2) Immediately beneath the cinder fill, fine-grained sediments from the cinders have been illuviated (washed down) into the underlying soil, also resulting in high zinc values of those samples.
3) Soluble and insoluble salts of zinc and the other metals may be temporarily stored in the aerated zone waiting for eventual migration downward with later recharge events. This also results in higher zinc concentrations in soil samples from this horizon.

As the Cation Exchange Capacity of the soil is exhausted and sufficient depth is reached to eliminate the three factors just noted, the metals buildup in the soil slowly continues to advance deeper into the soil profile. As the exchange process occurs, calcium and magnesium are released into the water from the soil and the pH of the infiltrating fluid is lowered. As the pH increases, the formation of zinc precipitates results, and a sharp break or decrease in soil zinc content is noted. Samples of water collected after percolating through the cinder fill materials forming the sides of the disposal pit had measured pH values near 5. It can be assumed that the same pH was experienced by water filtering downward through the cinder fill covering the plant surface. It is suspected that sulfur contained in the cinders was dissolved to form a weak sulfuric acid, thus creating the low pH and increasing the mobility of the zinc.

Conclusions pertaining to the mechanism of zinc and other metals fixation drawn from this field study indicated that increased removal of metals from solution occurs with increasing pH values and with increasing concentrations of the heavy metal in solution.

Chemical analysis of water collected from deep wells at Site A showed less than 0.5 mg/l zinc. The zinc contents of water collected from the shallow wells tapping the Hagarstown sand unit were 10,000 mg/l near the scrubber sludge pit and decreased to 1 mg/l at the boundary of the plant property. Because the sampling procedure was not satisfactory and the attempt to detect well seal failures was unsuccessful, further analysis of the water quality data generated probably is not worthwhile. The sampling procedure used in this study could account for as much as 40 to 80 percent of the fluctuations noted between sampling periods.

To better define the quality of water in an affected and unaffected area, water samples were collected from wells in each area for total mineral analysis. The results of the analysis of a water sample from the shallow control hole well indicated general agreement for the unaffected area well. In the affected area well, increases in mineral constituents were observed. Also, the zinc concentration (750 mg/l) and pH (6.5) were in excellent agreement with the solubility of zinc (800 mg/l at 6.5pH). Evidence of ion exchange was shown by the high concentrations of calcium (2400 mg/l) and magnesium (893 mg/l). The cation exchange positions in soils in this region of Illinois are principally filled with calcium and lesser amounts of magnesium. Zinc is higher in the montmorillonite exchange series than Ca and Mg and thus will replace these ions on the clay structure. This process releases calcium and magnesium to the environment, even when these are not part of the original waste stream.

Because of these phenomena, it is recommended that total mineral analysis be conducted on water samples from monitoring wells where cation exchange is likely to occur. Increases in one or more of these constituents could be an early warning of the eventual appearance of more toxic metals. However, to interpret a series of samples properly, the problem associated with collecting comparative samples must be solved.

In attempting to evaluate the relative merits of soil sampling versus well installation and water samplings, the costs of analytical work and the results obtained should be considered. Depending on the type of waste to be disposed of or monitored, soil sampling may prove to be more effective even though more costly. If a research project is being conducted, coring would prove to be most useful. The coring and analyses of the core samples give a better understanding of the phenomena taking place in the soil. However, due to the costs, coring may not be practical as a routine monitoring technique.

Recommendations

On the basis of the results of this study we recommend the following:

1) Coring and soil analysis should be used in waste disposal research projects or in waste disposal operations when the toxicity of a waste product warrants the additional expenditure.
2) A limited number of core samples, soil analyses, and geologic interpretations are advisable for evaluating alternative disposal sites. Soil analyses provide a better understanding of soil interaction with the waste product than is otherwise possible, and geologic interpretation of the core samples provides better information for design and location of monitoring wells.
3) Routine monitoring of most disposal sites should be accomplished with wells located and designed on the basis of preliminary coring analysis. Periodic coring and soil analysis may be worthwhile to substantiate original soil effectiveness assumptions.

The full report was submitted in partial fulfillment of Grant No. R803216 by the Illinois State Geological Survey and the Illinois State Water Survey under the sponsorship of the U.S. Environmental Protection Agency. The report, entitled "Retention of Zinc, Cadmium, Copper, and Lead by Geologic Materials," was published as Cooperative Groundwater Report 9 by the Illinois State Water Survey and the Illinois State Geological Survey.

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The complete report, entitled "Retention of Zinc, Cadmium, Copper, and Lead by Geologic Materials," (Order No. PB 83-232 819; Cost: $18.95, subject to change) will be available only from:
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